

PATENT SPECIFICATION

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(54) ACRYLONITRILE-BUTADIENE-STYRENE POLYMERS HAVING IMPROVED RESISTANCE TO DISCOLORATION

*dry blending
w/epoxy 21*

(71) We, ARGUS CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 633 Court Street, Brooklyn, New York, 11231, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to acrylonitrile-butadiene-styrene polymers having improved resistance to discolouration.

Acrylonitrile-butadiene-styrene polymers, also known as ABS polymers, have a tendency to develop a dark discolouration when heated at the temperatures necessary to process them, such as during molding and calendering. This discoloration is not masked even when pigments are added, although the pigment does to some extent hide a slight off-color.

The development of this discoloration is generally associated with a decomposition or degradation undergone by the polymer at elevated temperatures, of the order of 300° to 375° F. The addition of any of a number of stabilizers have been proposed, to overcome this tendency.

Cummings, U.S. patent No. 3,267,069, dated August 16, 1966, describes stabilizer combinations comprising a mixture of zinc sulfide and an ester of thiodipropionic acid, to which can also be added organic phosphites, polyhydric polycyclic phenols, and organic amines.

Hecker and Abramoff, U.S. patent No. 3,472,813, patented October 14, 1969, suggest combinations of alkyl polyphosphate salts and polyhydric polycyclic phenols, to which can also be added organic phosphites of the type described in U.S. patent No. 3,244,650, dated April 5, 1966, to Hecker et al.

Societa Edison, Netherlands patent application No. 64/11 434, published April 12, 1965, describes the addition of epoxy fatty acid esters as a plasticizer to acrylonitrile-styrene-butadiene polymers to improve molding without thermal degradation. Combinations of the epoxy fatty acid ester as plasticizer with lead salts and acid phosphites as stabilizers are suggested.

One of the problems with the stabiliser combinations in use heretofore is that they are effective either with an unpigmented or with a pigmented acrylonitrile-butadiene-styrene polymer, but not with both. This means that the formulator must use two different types of stabiliser compositions, according to whether the polymer that he wishes to stabilise is pigmented or unpigmented.

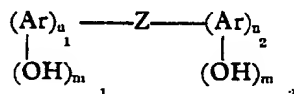
In accordance with the instant invention, it has been determined that stabiliser systems comprising an organic phosphite, a polyhydric polycyclic phenol, and an epoxy compound are capable of enhancing the resistance to discoloration of both pigmented and unpigmented acrylonitrile-butadiene-styrene polymers when heated at elevated temperatures of from 300° to 375°F and higher. These stabiliser combinations display an enhanced stabilising effectiveness, that is greater than that displayed by any of the stabiliser components, taken separately or in pairs. Evidently, these components complement each other in an unusual manner, and relative lack of effectiveness of the epoxy

[P.]

compound, taken alone, or in combinations with the phosphite or the phenol, makes the overall enhanced effectiveness of the three-component combination in both pigmented and unpigmented polymer all the more surprising.

Accordingly the present invention provides an acrylonitrile-butadiene-styrene polymer having its resistance to deterioration when heated at 350°F and above enhanced by an amount of from 0.1 to 10% by weight of the polymer of a stabiliser combination comprising a polyhydric polycyclic phenol, an organic phosphite, and an epoxy compound the organic phosphite and epoxy compound each being in an amount of from 2.5 to 50 parts by weight, and the phenol being in an amount of from 0.5 to 50 parts by weight, the amount of each being selected within such ranges to enhance the stabilising effectiveness of the others.

The polyhydric polycyclic phenols employed in the three component stabiliser combinations used, the invention include aromatic nuclei which are linked by a polyvalent linking radical and are defined by the formula:



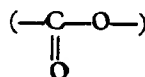
wherein Z is a polyvalent linking group selected from an oxygen or sulfur atom or an aliphatic, cycloaliphatic, or aromatic hydrocarbon; oxyhydrocarbon; thiohydrocarbon; heterocyclic; carbonyl; sulfinyl; or sulfonyl groups, and has up to twenty carbon atoms.

Ar is a phenolic nucleus which can be a phenyl or a polycarbocyclic group having condensed or separate phenyl rings; each Ar group contains at least one free phenolic hydroxyl group up to a total of four, m_1 and m_2 are numbers from one to four, and n_1 and n_2 are numbers, one or greater, and preferably from one to four. The Ar rings can also include additional rings connected by a bivalent linking nucleus of the type Z, for example, Ar—Z—Ar—Z—Ar.

The aromatic nucleus Ar can, in addition to phenolic hydroxy groups, include one or more inert substituents. Examples of such inert substituents include halogen atoms, e.g. chlorine, bromine and fluorine; organic radicals containing from one to thirty carbon atoms, such as alkyl, aryl, alkenyl, alkaryl, aralkyl, cycloalkenyl, cycloalkyl, alkoxy, aryloxy and acyloxy groups ($\text{R}'\text{C}=\text{O}$) where R' is aryl, alkyl or cycloalkyl, or



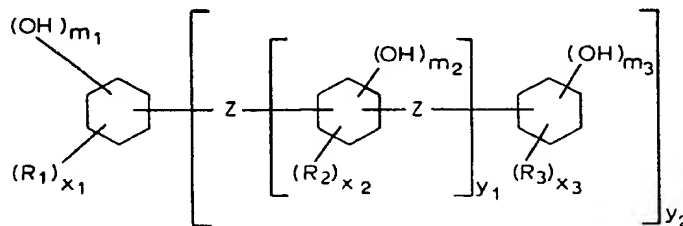
thio hydrocarbon groups having from one to thirty carbon atoms, and carboxyl



groups. Usually, however, each aromatic nucleus will not have more than eighteen carbon atoms in any hydrocarbon substituent group per nucleus.

Typical aromatic nuclei include phenyl, naphthyl, phenanthryl, triphenylenyl, anthracenyl, pyrenyl, chrysenyl, and fluorenyl groups.

The simplest form of polyhydric polycyclic phenol has the structure:

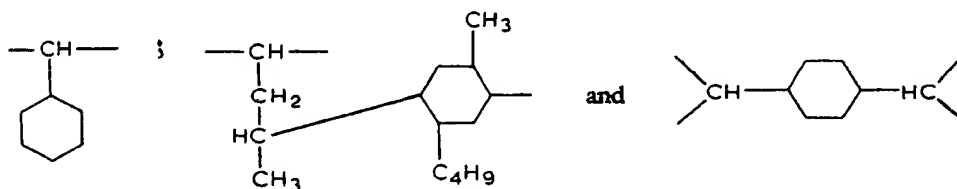


wherein R_1 , R_2 and R_3 are inert substituent groups as set forth above, m_1 and m_3 are integers from one to a maximum of five, m_2 is an integer from one to a maximum of four, x_1 and x_3 are O or integers from one to four, and x_2 is O or an integer from one to three; y_1 can be O or an integer from one to six and y_2 can be an integer from one to five, preferably one or two.

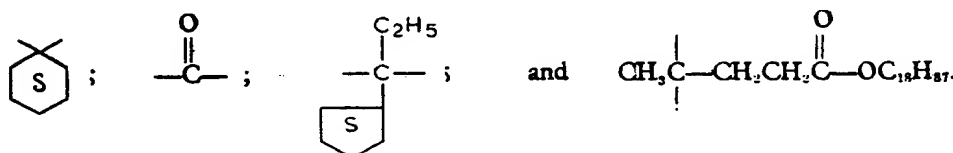
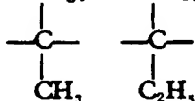
Preferably, the hydroxyl groups are located ortho and/or para to Z, and there is only one hydroxyl group per phenyl nucleus.

Exemplary Z groups are alkylene, alkylidene, alkenylene, arylalkylene, aralkylidene, cycloalkylene and cycloalkylidene, and oxa- and thio-substituted such groups, carbonyl groups, tetrahydrofuranes, esters and triazino groups. The Z groups are usually bi-, tri-, or tetravalent, connecting two, three or four Ar groups. However, higher valence Z groups, connecting more than four Ar groups, can also be used. According to their constitution the Z groups can be assigned to subgenera as follows:

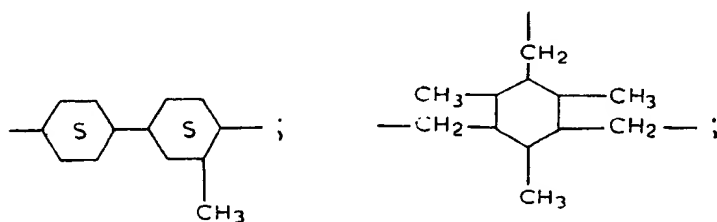
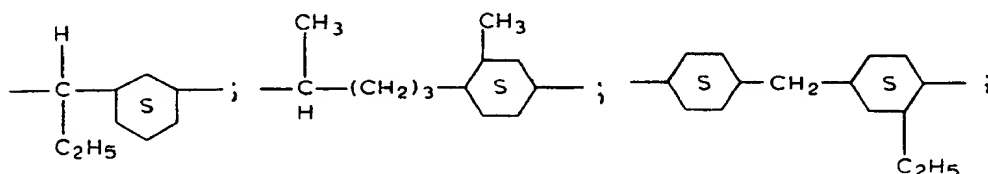
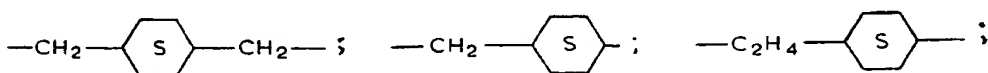
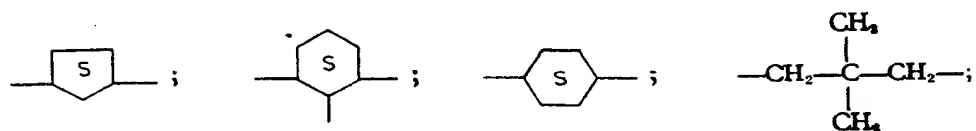
1) Z groups made up of a single carbon carrying at least one hydrogen with other substituents linking two Ar nuclei, such as $-\text{CH}_2-$; $-\text{CH}-$;

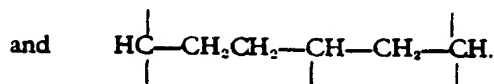


2) Z groups made up of a single carbon carrying only substituents other than hydrogen, such as CH_3 ; CH_3 ;

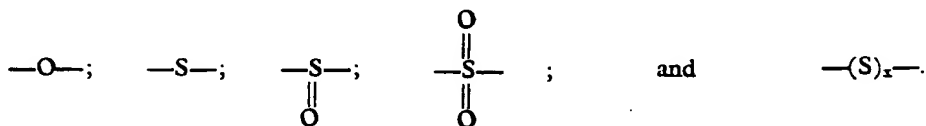


3) Z groups where at least two carbons connect the aromatic groups in an open-chain or cyclic arrangement, such as

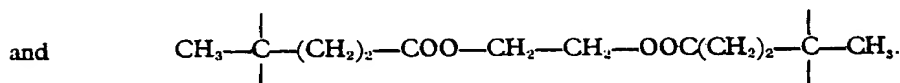
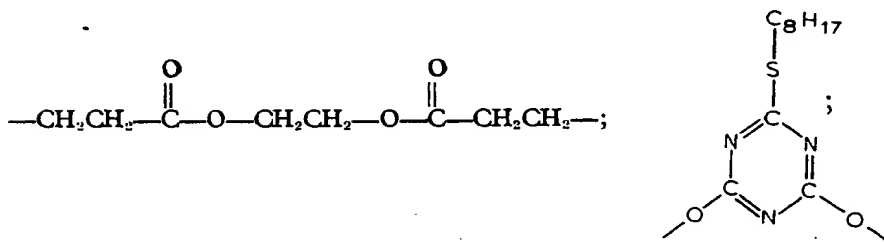
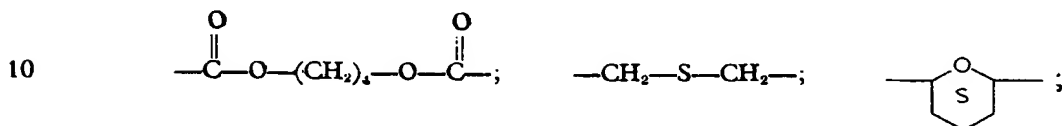
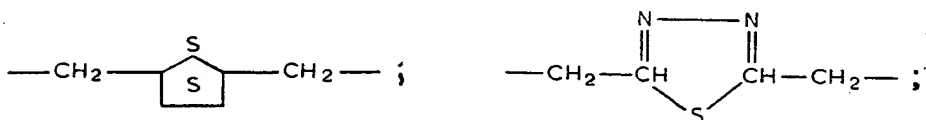
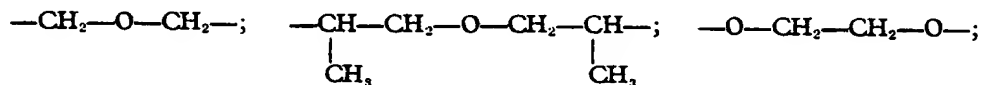




4) Z groups where only atoms other than carbon link the aromatic rings, such as



5) Z groups made up of more than a single atom including both carbon and other atoms linking the aromatic nuclei, such as:



Exemplary polyhydric polycyclic phenols used in accordance with the invention are 4,4' - methylenebis - (2 - tertiary - butyl - 5 - methyl - phenol), 2,2' - bis(4-hydroxyphenyl) propane, methylenebis - (p - cresol), 4,4' - oxobis - phenol, 4,4' - oxobis(3 - methyl - 5 - isopropyl - phenol), - 4,4' - oxobis(3 - methyl - phenol), 2,2' - oxobis(4 - dodecyl - phenol), 2,2' - oxobis(4 - methyl - 5 - tertiary - butyl - phenol), 4,4' - n - butylidenebis - (2 - t - butyl - 5 - methyl - phenol), 2,2' - methylenebis - [4 - methyl - 6, (1 - methyl - cyclohexyl) - phenol], 4,4' - cyclohexylidenebis(2-tertiary - butyl - phenol), 2,6 - bis - (2' - hydroxy - 3' - t - butyl - 5' - methyl - benzyl) - 4 - methyl - phenol, 4,4' - oxobisnaphthalene - 5,5 - diol, 1,2' - methylenebis - naphthalene - 1,8 - diol, 1,3' - bis(naphthalene - 2,5 - diol)propane, and 2,2' - butylidene bis(naphthalene-2,7-diol), di(hydroxyphenyl) ketone, (3-methyl-5-tert-

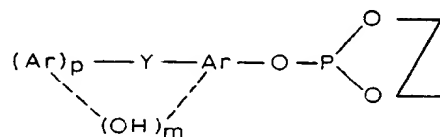
butyl - 4 - hydroxy - phenyl) - 4' - hydroxyphenyl)methane, 2,2' - methylenebis(4-methyl - 5 - isopropylphenol), 2,2' - methylenebis(5 - tert - butyl - 4 - chloro - phenol), (3,5 - di - tert - butyl - 4 - hydroxyphenyl) - (4' - hydroxy - phenyl)methane, (2-hydroxy - phenyl) - (3' - 5' - di - tert - butyl - 4' - hydroxyphenyl)methane, 2,2'-ethylidenebis(4 - octylphenol), 4,4' - isopropylidenebis(2 - tert - butyl - phenol), 2,2' - isobutylidenebis - (4 - nonylphenol), 2,4 - bis(4 - hydroxy - 3 - t - butylphenoxy)-6 - (n - octylthio) - 3,3,5 - triazine, 2,4,6 - tris(4 - hydroxy - 3 - t - butylphenoxy)-1,3,5 - triazine, 2,2' - bis(3 - methyl - 5 - t - butyl - 4 - hydroxyphenyl) - thiazolo-(5,4 - d) - thiazole, 4,4' - bis(4 - hydroxy - phenyl)pentanoic acid octadecyl ester, cyclopentylidene 4,4' - bisphenol, 2 - ethylbutylidene 4,4' - bisphenol, 4,4' - cyclooctylidenebis(2 - cyclohexylphenol), β,β - thiodiethanolbis(3 - tert - butyl - 4 - hydroxyphenoxy acetate), 1,4 - butanediolbis(3 - tert - butyl - 4 - hydroxyphenoxy acetate), pentaerythritoltetra - (4 - hydroxyphenol - propionate), 2,4,4' - trihydroxy - benzophenone, bis(2 - tert - butyl - 3 - hydroxy - 5 - methylphenyl) sulfide, bis(2 - tert - butyl - 4 - hydroxy - 5 - methylphenyl) sulfide, bis(2 - tert - butyl - 4 - hydroxy - 5 - methylphenyl) sulfoxide, bis(3 - methyl - 5 - tert - butyl - 4 - hydroxy benzyl) sulfide, bis(2-hydroxy - 4 - methyl - 6 - tert - butyl phenyl) sulfide, 4,4' - bis(4 - hydroxyphenyl)-pentanoic acid octadecyl thiopropionate ester, 1,1,3 - tri(2' - methyl - 4' - hydroxy-5' - tert - butylphenyl)butane, 1,1,3 - tris (1 - methyl - 3 - hydroxy - 4-tert - butylphenyl) butane, 1,8 - bis(2 - hydroxy - 5 - methylbenzoyl) - n - octane, 2,2' - methylene - bis - [4' - (3 - tert - butyl - 4 - hydroxyphenyl) - thiazole], (1-methyl - 3 - (3 - methyl - 5 - tert - butyl - 4 - hydroxybenzyl) naphthalene), 2,2' - (2-butene)bis-(4-methoxy-6-tert-butyl phenol).

The polyhydric polycyclic phenols used in the invention can also include condensation products of phenol or alkyl phenols with aldehydes, for example formaldehyde, acetaldehyde, and propionaldehyde, or with ketones, for example, acetone.

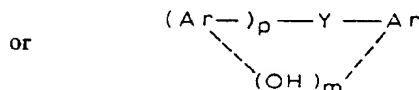
The polyhydric polycyclic phenols used in the invention can also be condensation products of phenol or alkyl-phenols with hydrocarbons having a bicyclic ring structure and a double bond or two or more double bonds, such as α -pinene, β -pinene, di-pentene, limonene, vinylcyclohexene, dicyclopentadiene, alloocimene, isoprene, and butadiene. These condensation products are usually obtained under acidic conditions in the form of more or less complex mixtures of monomeric and polymeric compounds. However, it is usually not necessary to isolate the individual constituents. The entire reaction product, merely freed from the acidic condensation catalyst and unchanged starting material, can be used with excellent results. While the exact structure of these phenolic condensation products is uncertain, the Z groups linking the phenolic nuclei all fall into subgenus 3. For methods of preparation see U.S. patent No. 3,124,555, U.S. patent No. 3,242,135, and British patent No. 961,504.

The alkyl, aryl, aryl alkyl, alkyl aryl, cycloalkyl, alkyl cycloalkyl, and cycloalkyl alkyl organic phosphites contain a total of from one to three groups selected from aryl, alkyl, and cycloalkyl groups having from one to thirty carbon atoms. The positions not substituted by organic groups contain hydrogen atoms. These groups may be present in any combination. Exemplary are triphenyl phosphite, tricresyl phosphite, tri(dimethylphenyl) phosphite, tri-n-butyl phosphite, triisooctyl phosphite, tridodecyl phosphite, diisooctyl phenyl phosphite, isooctyl diphenyl phosphite, tri(p-t-octylphenyl) phosphite, tri(p - t - nonylphenyl) phosphite, tri(p - t - nonyl - o - cresyl) phosphite, tri(p - t - nonylphenyl)phosphite, tri(p - t - nonyl - o - cresyl) phosphite, tribenzyl phosphite isobutyl dicresyl phosphite, isooctyl di(p-t-octylphenyl) phosphite, tri(2-ethylhexyl) phosphite, tri(2-cyclohexylphenyl) phosphite, trialpha-naphthyl phosphite, tri(di-phenyl) phosphite, tri(2-phenyl-ethyl)phosphite, tricyclohexyl phosphite, and tricyclopentyl phosphite.

Also useful are the polycyclic phenolic phosphites defined by the formula:



wherein Z is selected from a hydrogen atom or an aliphatic, cycloaliphatic, aromatic



group, taken in sufficient number to satisfy the valences of the two phosphite oxygen atoms; the dotted line indicating that the hydroxyl group is optionally attached to either of the Ar substituents. At least one Z group is an aliphatic or cycloaliphatic group.

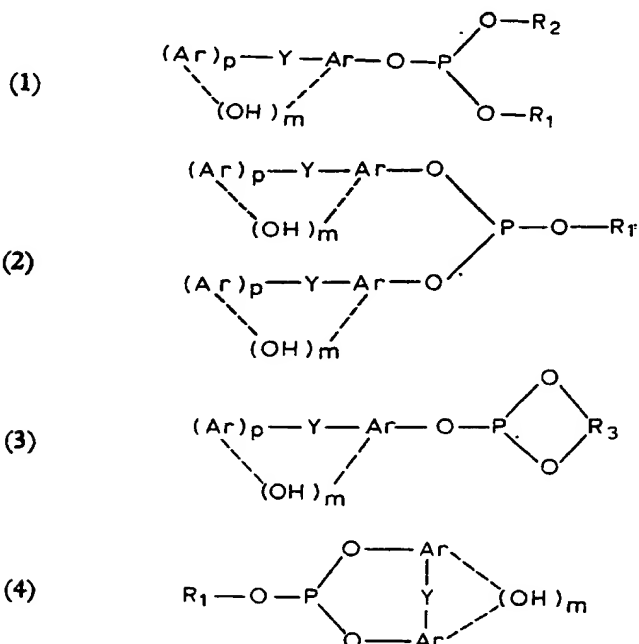
5 m is a number from one to five, and p is a number from one to four.

Y is a polyvalent linking group selected from an oxygen or sulfide sulfur (S)_x, where x is a number from one to five, linked directly to Ar or via aliphatic, cycloaliphatic and aromatic hydrocarbon groups attached to the Ar group; oxaliphatic; thioaliphatic; oxycycloaliphatic, thiocycloaliphatic; heterocyclic; oxyheterocyclic, thioheterocyclic, carbonyl, sulfinyl, and sulfonyl groups.

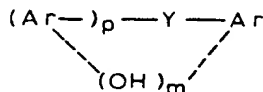
10 The Ar group can be any aromatic nucleus, monocarbocyclic or polycarbocyclic, with condensed or separate rings, and the rings when separate can also be connected by a bivalent linking nucleus of the type of Y, for example,



15 Exemplary of types of phosphites falling within the above general formula are the following:

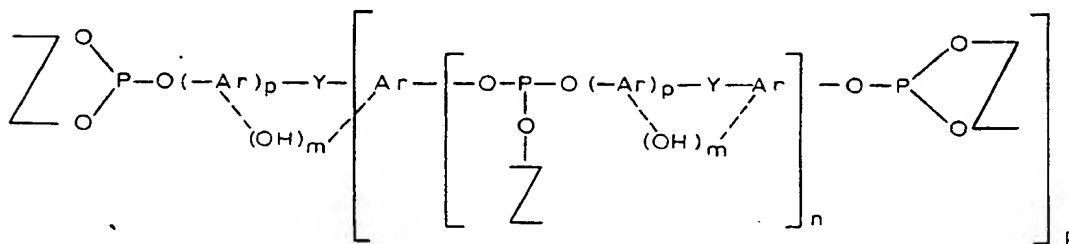


In the above formulae, R₁ is a monovalent aliphatic or cycloaliphatic group, R₂ is a monovalent aliphatic, cycloaliphatic, aromatic or heterocyclic group, and R₃ is a bivalent aliphatic or cycloaliphatic group. Any



25 groups can be cross-linked to other phosphite groups.

The polymeric organic phosphite esters have the general formula:

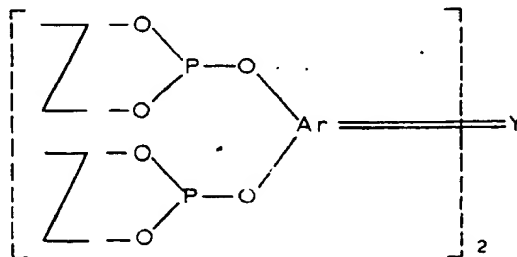
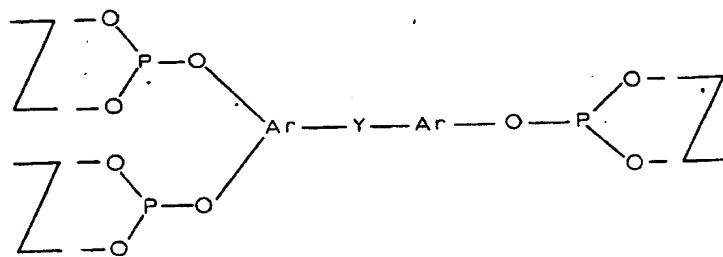
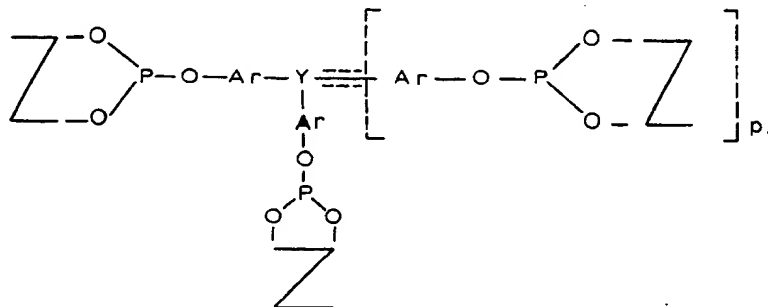


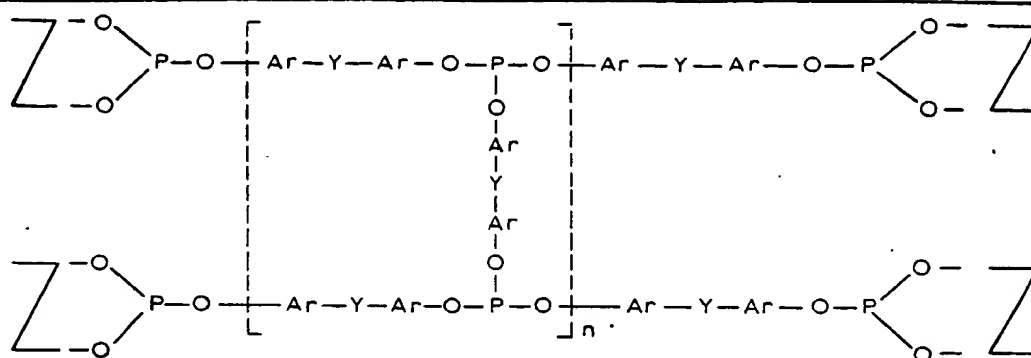
wherein n, p, Ar and Y are as defined above, and at least one of the Z's is a cycloaliphatic group, the aliphatic and cycloaliphatic groups being present in sufficient number to impart an enhanced stabilizing effectiveness for polyvinyl chlorid and polyolefin resins to the phosphite, and n and p, represent the number of such bracketed repeating units in each chain, and can range from zero to an indefinite upper limit, depending upon the molecular weight of the polymer. Inasmuch as compatibility with the synthetic resin may decrease at very high values of n, when the polymers tend to become resinous in nature, usually n does not exceed ten, and preferably does not exceed five.

Z can be monovalent or polyvalent, inasmuch as Z can be a plurality of radicals taken separately to satisfy the valences of the phosphite oxygen atoms to which Z is attached. Furthermore, Z can be a bivalent radical forming a heterocyclic ring with the oxygen atoms, or when present in the repeating unit can form a cross-link to adjacent polyphosphite chains of like type. Thus, Z when bivalent can be an aliphatic bivalent group, an aromatic bivalent group, a cycloaliphatic bivalent group and a heterocyclic bivalent group. Z when monovalent can include an aliphatic, cycloaliphatic, aromatic or heterocyclic group.

It will be apparent that when p is one and the Z radicals present in the repeating unit of the polymeric phosphite are monovalent, the polyphosphites exist as linear chains, and when the Z radicals in the repeating units are bivalent cross-links, the polyphosphites take the form of cross-linked polymers.

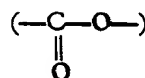
The polyphosphites which exist as cross-linked polymers wherein the Z of the repeating unit is a cross-link to an adjacent chain can take a variety of forms, only some of which because of space limitations can be represented here. The following formulae are exemplary of cross-linked polymers:





In all of the above formulae, the Z groups normally have a total of from one to thirty carbon atoms, and preferably from two to ten carbon atoms. Z groups when bivalent usually have at least two carbon atoms where they form a heterocyclic ring with two oxygen atoms of a phosphite group, n and p₁ are numbers greater than zero and preferably from one to three.

The aromatic nucleus Ar can in addition to phenolic hydroxyl groups include one or more inert substituents. Examples of such inert substituents include halogen atoms, e.g. chlorine, bromine and fluorine; hydrocarbon groups (such as alkyl or cycloalkyl groups) having from one to thirty carbon atoms; oxy- or thio-hydrocarbon groups having from one to thirty carbon atoms, carbonyl (C=O) and carboxyl

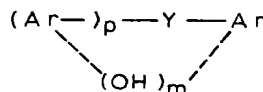


groups. Usually, however, each aromatic nucleus will not have more than eighteen carbon atoms in any hydrocarbon substituent group. The Ar group can have from one to four substituent groups per nucleus.

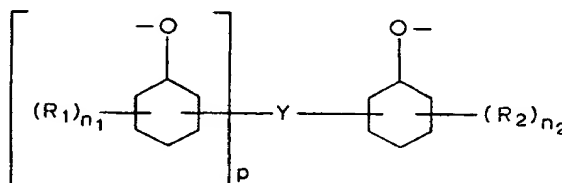
Typical aromatic nuclei include phenyl, naphthyl, phenanthryl, triphenylenyl, anthracenyl, pyrenyl, chrysenyl, and fluorenyl groups.

In these phosphites there can be none or from one phenolic hydroxyl group or residue thereof for each aromatic ring, up to five hydroxyl groups per ring.

In one form the



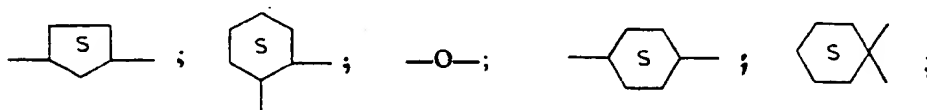
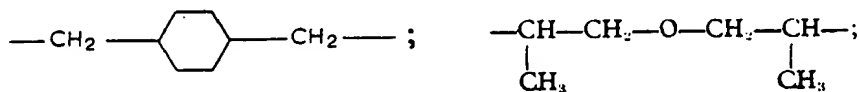
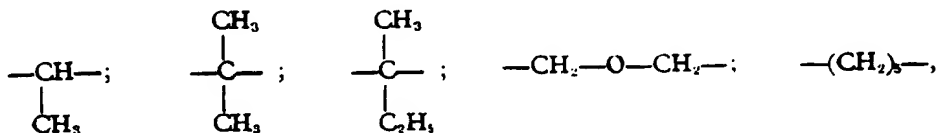
group has the structure:



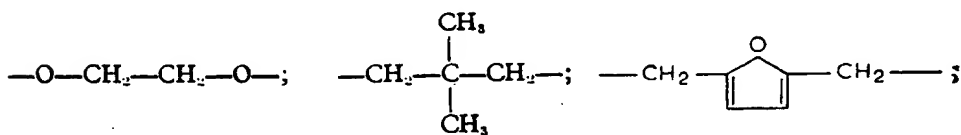
R₁ and R₂ represent hydroxyl groups or the inert substituents set forth above, p is as defined above and n₁ and n₂ represent the number of R groups on each ring, and have a value from zero to four.

Exemplary Y groups are alkylene, alkylidene, alkenylene, arylkylene, aralkylidene, cycloalkylene and cycloalkylidene, and oxy-, and thio-substituted such groups, carbonyl, tetrahydrofuranes, esters and triazino groups. The Y groups are usually bi-, tri-, or tetravalent, connecting two, three or four Ar groups. However, higher valence Y groups, connecting more than four Ar groups, can also be used.

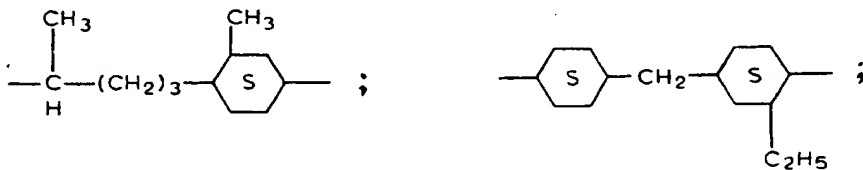
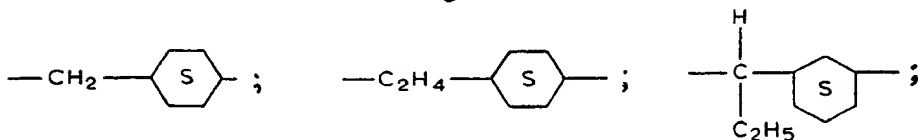
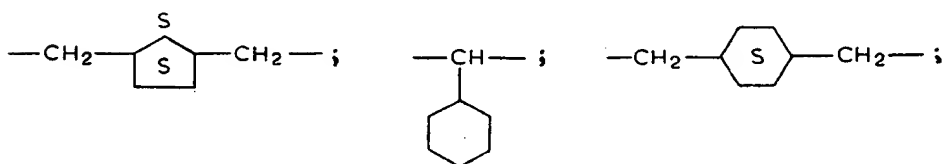
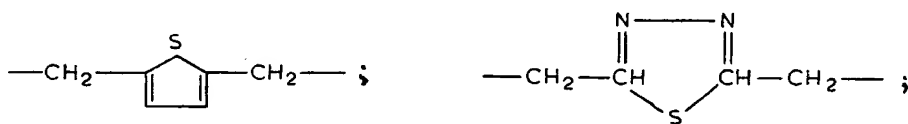
Examples of Y are: $-\text{CH}_2-$; $-\text{CH}_2\text{CH}_2-$;



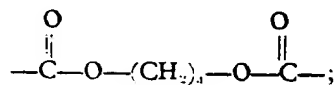
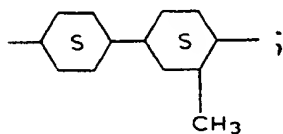
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total number of carbon atoms of the acid and the alcohol being within the range stated. Typical monohydric alcohols include butyl alcohol, 2-ethyl hexyl alcohol, lauryl alcohol, isoocetyl alcohol, stearyl alcohol, and oleyl alcohol. The octyl alcohols are preferred. Typical polyhydric alcohols include pentaerythritol, glycerol, ethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, neopentyl glycol, ricinoleyl alcohol, erythritol, mannitol and sorbitol. Glycerine is preferred. These alcohols may be fully or partially esterified with the epoxidized acid. Exemplary are epoxidized 1,4-butylene glycol diacrylate and epoxidized pentaerythritol tetratallate. Also useful are the epoxidized mixtures of higher fatty acid esters found in naturally-occurring oils such as epoxidized cottonseed oil, epoxidized tall oil fatty acid esters, epoxidized coconut oil and epoxidized tallow. Of these, epoxidized soybean oil is preferred.

The alcohol can contain the epoxy group and have a long or short chain, and the acid can have a short or long chain, such as epoxy stearyl acetate, epoxy stearyl stearate, glycidyl stearate, and polymerized glycidyl methacrylate.

The stabilizer combinations used in the invention are effective with acrylonitrile-butadiene-styrene polymers as a class. Many of the ABS polymers available commercially are prepared by dispersing an elastomeric phase such as a diene homopolymer, such as polybutadiene, into a rigid styrene-acrylonitrile copolymer or a terpolymer. The elastomeric phase can also be a copolymer with a styrene or acrylonitrile, or a styrene acrylonitrile graft on an elastomeric substrate, such as polybutadiene. The contribution of the acrylonitrile, styrene and butadiene is each important. Terpolymers of the three monomers do not always have the desired properties, and ABS graft copolymers are most common, and include a styrene acrylonitrile copolymer phase and a preformed polybutadiene substrate on which is grafted styrene and acrylonitrile, usually by emulsion, bulk or suspension polymerization. See *Chemistry and Industry*, August 13, 1966, pages 1399-1405. All of these are encompassed herein under the terms "acrylonitrile-butadiene-styrene polymer", or "ABS polymer".

ABS polymers generally contain from 15 to 35% acrylonitrile, from 5 to 35% butadiene, and from 40 to 80% styrene, by weight. The matrix usually has a molecular weight of from 200,000 to 450,000 or more, and a density of from 0.99 to 1.09 g/cc.

The acrylonitrile portion of the ABS polymer imparts chemical resistance to the polymer; the styrene portion of the ABS polymer imparts good fabrication characteristics to the polymer; and the rubber or butadiene portion of the ABS polymer provides the rubberiness and toughness to the polymer. Accordingly, chemical resistance, good fabrication characteristics, and rubberiness and toughness features can be varied in any given ABS polymer by varying the quantities of the acrylonitrile, butadiene and styrene. For example, the impact strength of the ABS polymer can be increased by increasing the amount of butadiene in the polymer. However, increase in impact strength is accompanied by slight reduction in heat resistance, rigidity, electrical properties and some of the other strength properties.

Heat-resistance properties of the ABS polymer can be improved by increasing the amount of acrylonitrile in the polymer. However, increased heat resistance, such as increasingly high heat-distortion temperatures, usually is accompanied by decreased impact strength, especially at low temperatures. Increasingly good fabrication characteristics of the polymer are obtained where larger quantities of styrene are used. However, such an ABS polymer usually has lower impact strength. Accordingly, the impact strength of ABS polymer at 73°F. varies from 9 ft.-lb./in. notch in extra high and low temperature impact grades, to 1.5 for medium impact grades.

The tensile strength of ABS polymer varies from 8800 psi for medium impact grades, with a tensile modulus of 400,000, to as low a tensile strength as 2400 psi, for a semi-flexible extrusion grade, and a tensile modulus of 2,100,000. The hardness of ABS polymer ranges from a Rockwell 118 for medium impact grade to a Rockwell 62 for a low temperature grade material. The range of deflection temperature for ABS polymer is from 230°F. at 264 psi and 240°F. at 66 psi., respectively, for heat resistant grades, to as low as 145°F. at 264 psi and 202°F. at 66 psi, respectively, with most commercial grades falling in the upper end of the range.

ABS polymer can be prepared by polymerizing acrylonitrile monomer and styrene monomer in a previously prepared polybutadiene latex, or butadiene copolymer rubber latex, under such conditions that an appreciable portion of the acrylonitrile and styrene become grafted or polymerized directly on the polybutadiene molecules. The polybutadiene portion or base portion of the ABS graft polymer molecule is rubbery, while the acrylonitrile and styrene grafted comonomer portions of the graft polymer molecule are resinous. See U.S. Patent No. 2,820,773 dated January 21, 1958, to Childers and Fisk for a detailed description of the graft polymerization technique for forming ABS polymer.

ABS polymer can also be prepared by blending styrene-acrylonitrile copolymer resins with butadiene-based elastomers, such as is described in U.S. Patent No. 2,439,902, dated April 6, 1948 to Daly, and No. 2,600,024, dated June 10, 1952, to Romeyn et al.

5 In addition, ABS graft copolymer can be physically blended with additional quantities of separately prepared resin, for example, styrene-acrylonitrile resin, with or without additional separately prepared butadiene-acrylonitrile copolymer rubber. See U.S. Patent No. 2,802,808 dated August 13, 1957 to Hayes for a complete description of the preparation of ABS polymer from ternary blends containing a resin, for example, 10 a copolymer of styrene for α -methylstyrene with acrylonitrile or methacrylonitrile; a rubber, for example, polybutadiene or butadiene copolymer; and a graft copolymer of styrene-acrylonitrile and butadiene.

Mixtures of ABS polymers with other compatible polymers, (for example, the polycarbonate of 4,4'-isopropylidene-bisphenol) and copolymers of acrylonitrile, or 15 methacrylonitrile, butadiene, and styrene, such as acrylonitrile-styrene, butadiene-styrene, and butadiene-acrylonitrile rubber, the ABS polymer being present in a sufficient amount, usually a major amount, that is 85% by weight or more, to present the stabilization problem resolved by the invention, can also be stabilized.

20 Furthermore, the styrene monomer of the ABS polymer can be replaced in whole or in part by α -methylstyrene in order to improve the heat distortion temperatures of the ABS polymer. Similarly, methyl methacrylate can be used in place of some of the acrylonitrile.

All of the above polymers fall within the term "ABS polymer", as used herein. Typical available ABS polymers and their physical properties are:

TABLE A

*CYCOLAC ABS POLYMERS

Grade and Characteristics	Condition	Units	ASTM Test Method	GS	T	X-27
Properties Reported values pertain only to natural resins; pigmenting may vary the properties				Maximum Toughness With High Modulus	Toughness With High Flow	Maximum High Heat With High Modulus
				GSM Injection and Blow Molding	Injection Molding	Injection Molding
				GSE Extrusion	Extrusion	
Mechanical						
Izod Impact Strength, unnotched $\frac{1}{8}$ " bar (2)	73°F	ft.-lbs./in. notch	D-256-56 Method A	29.3	26.0	33.0
	73°F			6.2	5.3	3.1
	-20°F			2.6	2.1	1.3
	-40°F			2.1	1.8	1.0
Charpy Impact Strength, unnotched $\frac{1}{4}$ " bar (1)	73°F	ft.-lbs./in. notch	D-256-56 Method B	35.0	26.0	19.3
	73°F			4.7	3.7	1.9
	-20°F			2.6	2.1	1.1
	-40°F			2.2	1.7	0.9
Tensile Strength, Type I $\frac{1}{8}$ " thickness (2)	160°F	psi	D-638-61T 0.2"/min.	3,400	3,200	4,600
	73°F			5,900	6,000	7,300
	-40°F			9,200	9,500	11,500
Tensile Modulus, Type I $\frac{1}{8}$ " thickness (2)	73°F	psi	D-638-61T 0.2"/min.	310,000	300,000	390,000
Flexural Strength $\frac{1}{8}$ " x 1" x 4" bar (1)	160°F, 73°F and -40°F	psi	D-790-61 0.05"/min.	No failure	No failure	No failure
Flexural Yield Strength $\frac{1}{8}$ " x 1" x 4" bar (1)	160°F	psi	D-790-61 0.05"/min.	5,700	5,500	7,500
	73°F			9,700	9,600	11,800
	-40°F			15,200	15,100	18,800
Flexural Modulus $\frac{1}{8}$ " x 1" x 4" bar (1)	160°F	psi	D-790-61 0.05"/min.	220,000	210,000	310,000
	73°F			320,000	320,000	400,000
	-40°F			360,000	360,000	460,000
Hardness $\frac{1}{8}$ " thickness (1)	73°F	Rockwell R	D-785-62 Method A	103	104	112

TABLE A (continued)

*CYCOLAC ABS POLYMERS

Grade and Characteristics	Condition	Units	ASTM Test Method	GS	T	X-27
Properties Reported values pertain only to natural resins; pigmenting may vary the properties				Maximum Toughness With High Modulus	Toughness With High Flow	Maximum High Heat With High Modulus
Wear Index, Taber Volume Loss Method CS-17 Wheel, 1000g. weight	73°F 50% R.H.	%		GSM Injection and Blow Molding	Injection Molding	Injection Molding
Deformation Under Load (1)		%		GSE Extrusion		Extrusion
Thermal Coefficient of Linear Thermal Expansion	24 hr., 122°F 2000 psi	%	D-621-59	19.2	18.8	0.21
Deflection Temperature, Unannealed $\frac{1}{8}$ " \times $\frac{1}{4}$ " \times 5" bar (1)	264 psi 66 psi zero load	in./in./°C. in./in./°F.	D-696-44 Calculated	9.5×10^{-3} 5.3×10^{-3}	9.5×10^{-3} 5.3×10^{-3}	6.0×10^{-3} 3.3×10^{-3}
Deflection Temperature, Annealed $\frac{1}{8}$ " \times $\frac{1}{4}$ " \times 5" bar (1)	264 psi 66 psi zero load	°F. at 10 mils Deflection °F. at 10 mils Deflection	D-648-56 D-648-56	193 211 221	192 209 220	226 238 250
Thermal Conductivity		BTU/hr./ft. ² /°F./in. Cal/Sec/cm ² /°C/cm.	C-177-45	1.55 5.45×10^{-4}	1.54 5.30×10^{-4}	2.38 8.18×10^{-4}
Flammability $\frac{1}{8}$ " \times $\frac{1}{4}$ " \times 5" bar (1)		in./min.	D-635-63	1.5	1.5	1.8
Analytical Specific Gravity (1)	73°F	%	D-792-60T Method A	1.04	1.04	1.06
Water Absorption (2)		%	D-570-63	0.43	0.40	0.36
Mold Shrinkage (2)		in./in.	D-955-51	0.006	0.005	0.004

*The word "CYCOLAC" is a Registered Trade Mark.

TABLE A

*CYCOLAC ABS POLYMERS

Grade and Characteristics	Condition	Units	ASTM Test Method	X-17 Maximum High Heat With Good Moldability	X-7 High Heat With Toughness	H Good Toughness
Properties Reported values pertain only to natural resins; pigmentation may vary the properties						
Mechanical Izod Impact Strength, unnotched $\frac{1}{8}$ " bar (2)	73°F 73°F -20°F -40°F	ft.-lbs./in. notch	D-256-56 Method A	2.5 0.7	32.0 4.2 1.4 1.2	No break 6.3 2.8 2.6
Charpy Impact Strength, unnotched $\frac{1}{4}$ " bar (1)	73°F 73°F -20°F -40°F	ft.-lbs./in. notch	D-256-56 Method B		33.0 3.1 1.7 1.4	No Break 5.3 2.9 2.6
Tensile Strength, Type I $\frac{1}{8}$ " thickness (2)	160°F 73°F -40°F	psi	D-638-61T 0.2"/min.	7,200	4,000 6,900 10,400	2,400 4,700 7,200
Tensile Modulus, Type I $\frac{1}{8}$ " thickness (2)	73°F	psi	D-638-61T 0.2"/min.	380,000	330,000	230,000
Flexural Strength $\frac{1}{8}$ " x $1\frac{1}{2}$ " x $\frac{1}{4}$ " bar (1)	160°F, 73°F and -40°F	psi	D-790-61 0.05"/min.	No failure	No failure	No failure
Flexural Yield Strength $\frac{1}{8}$ " x $1\frac{1}{2}$ " x $\frac{1}{4}$ " bar (1)	160°F 73°F -40°F	psi	D-790-61 0.05"/min.	6,800 10,600 18,100	6,200 10,200 16,100	4,100 7,600 11,800
Flexural Modulus $\frac{1}{8}$ " x $1\frac{1}{2}$ " x $\frac{1}{4}$ " bar (1)	160°F 73°F -40°F	psi	D-790-61 0.05"/min.	270,000 380,000 420,000	260,000 360,000 390,000	160,000 240,000 280,000
Hardness $\frac{1}{8}$ " thickness (1)	73°F	Rockwell R	D-785-62 Method A	110	107	88

TABLE A (continued)

Grade and Characteristics		Condition	Units	ASTM Test Method	X-17	X-7	H
Properties Reported values pertain only to natural resins; pigmenting may vary the properties					Maximum High Heat With Good Moldability	High Heat With Toughness	Good Toughness
Wear Index, Taber Volume Loss Method CS-17 Wheel, 1000g. weight		73°F 50% R.H.	%		Injection Molding	Injection Molding	Injection Molding
Deformation Under Load (1)		24 hr., 122°F 2000 psi	%	D-621-59	Extrusion	Extrusion	Extrusion
Thermal Coefficient of Linear Thermal Expansion			in./in./°C. in./in./°F.	D-696-44 Calculated	6.2 × 10 ⁻³	8.2 × 10 ⁻³ 4.5 × 10 ⁻³	10.4 × 10 ⁻³ 5.8 × 10 ⁻³
Deflection Temperature, Unannealed ½" × ¼" × 5" bar (1)		264 psi 66 psi zero load	°F. at 10 mils Deflection	D-648-56	220	203 220 230	186 206 223
Deflection Temperature, Annealed ½" × ¼" × 5" bar (1)		264 psi 66 psi zero load	°F. at 10 mils Deflection	D-648-56	238	224 230 235	214 222 228
Thermal Conductivity			BTU/hr./ft. ² /°F./in. Cal/Sec/cm ² /°C/cm.	C-177-45		1.99 6.52 × 10 ⁻⁴	1.56 5.05 × 10 ⁻⁴
Flammability ½" × ¼" × 5" bar (1)			in./min.	D-635-63		1.4	1.4
Analytical Specific Gravity (1)		73°F		D-792-60T Method A	1.06	1.05	1.02
Water Absorption (2)		73°F	%	D-570-63		0.43	0.42
Mold Shrinkage (2)			in./in.	D-955-51	0.004	0.005	0.007

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TABLE A

*CYCOLAC ABS POLYMERS

Grade and Characteristics	Condition	Units	ASTM Test Method	L	CG	E
Properties Reported values pertain only to natural resins; pigmenting may vary the properties				Good Toughness At Low Temp.	Toughness With Low Gloss	Very High Impact At Low Temp.
Mechanical				Injection Molding	Injection Molding	Injection Molding
Izod Impact Strength, unnotched $\frac{1}{4}$ " bar (2)	73°F 73°F -20°F -40°F	ft.-lbs./in. notch	D-256-56 Method A	Extrusion No break 6.7 4.3 2.8	Extrusion No break 8.0 2.0	Extrusion No break 8.5 3.0
Charpy Impact Strength, unnotched $\frac{1}{4}$ " bar (1)	73°F 73°F -20°F -40°F	ft.-lbs./in. notch	D-256-56 Method B	No break 6.0 3.7 3.1		
Tensile Strength, Type I $\frac{1}{4}$ " thickness (2)	160°F 73°F -40°F	psi	D-638-61T 0.2"/min.	2,600 5,000 7,400	5,000 6,500	4,800
Tensile Modulus, Type I $\frac{1}{4}$ " thickness (2)	73°F	psi	D-638-61T 0.2"/min.	230,000	260,000	230,000
Flexural Strength $\frac{1}{4}$ " x $\frac{1}{4}$ " x 4" bar (1)	160°F, 73°F and -40°F	psi	D-790-61 0.05"/min.	No failure	No failure	No failure
Flexural Yield Strength $\frac{1}{4}$ " x $\frac{1}{4}$ " x 4" bar (1)	160°F 73°F -40°F	psi	D-790-61 0.05"/min.	4,300 7,800 12,100	3,500 7,200 10,500	7,300
Flexural Modulus $\frac{1}{4}$ " x $\frac{1}{4}$ " x 4" bar (1)	160°F 73°F -40°F	psi	D-790-61 0.05"/min.	160,000 250,000 180,000	140,000 260,000 300,000	230,000
Hardness $\frac{1}{4}$ " thickness (1)	73°F	Rockwell R	D-785-62 Method A	89	88	85

TABLE A (continued)

*CYCOLAC ABS POLYMERS

Grade and Characteristics	Condition	Units	ASTM Test Method	L	CG	E
Properties Reported values pertain only to natural resins; pigmenting may vary the properties				Good Toughness At Low Temp.	Toughness With Low Gloss	Very High Impact At Low Temp.
Wear Index, Taber Volume Loss Method CS-17 Wheel, 1000g. weight	73°F 50% R.H.	%		Injection Molding		Injection Molding
Deformation Under Load (1)		%		Extrusion	Extrusion	Extrusion
Thermal Coefficient of Linear Thermal Expansion	24 hr., 122°F 2000 psi	%	D-621-59	23.0		
Deflection Temperature, Unannealed $\frac{1}{4}'' \times \frac{1}{4}'' \times 5''$ bar (1)	264 psi 66 psi zero load	in./in./°C. in./in./°F.	D-696-44 Calculated	10.1×10^{-3} 5.6×10^{-3}	10.0×10^{-3}	188
Deflection Temperature, Annealed $\frac{1}{4}'' \times \frac{1}{4}'' \times 5''$ bar (1)	264 psi 66 psi zero load	°F. at 10 mils Deflection	D-648-56	187 210 224	190 214	
Thermal Conductivity		°F. at 10 mils Deflection	D-648-56	218 224 227	218 225	218
Flammability $\frac{1}{4}'' \times \frac{1}{4}'' \times 5''$ bar (1)		BTU/hr./ft. ² /°F./in. Cal/Sec/cm ² /°C/cm.	C-177-45	1.56 5.05×10^{-4}		
Analytical Specific Gravity (1)	73°F	in./min.	D-635-63	1.4		
Water Absorption (2) Mold Shrinkage (2)	73°F	% in./in.	D-792-60T Method A D-570-63 D-955-51	1.02 0.45 0.007	1.04	1.02

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TABLE A

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Properties Reported values pertain only to natural resins; pigmenting may vary the properties	Condition	Units	ASTM Test Method	CYCOLON MEDIUM IMPACT ABS POLYMERS			SPECIAL ABS RESINS
				A	AH	DH	
Mechanical Izod Impact Strength, unnotched $\frac{1}{8}$ " bar (2)	73°F	ft.-lbs./in. notch	D-256-56 Method A	AM For Injection Molding	High Heat	High Heat	EP-3510 Grey Only For Chrome Plated Parts
	73°F						
	-20°F						
	-40°F						
Charpy Impact Strength, unnotched $\frac{1}{8}$ " bar (1)	73°F	ft.-lbs./in. notch	D-256-56 Method B	AE For Extrusion	Injection Molding	Injection Molding	Injection Molding
	73°F						
	-20°F						
	-40°F						
Tensile Strength, Type I $\frac{1}{8}$ " thickness (2)	160°F	psi	D-638-61T 0.2"/min.	3,500 6,300 10,000	6,800	7,800	3,200 6,000 9,500
	73°F						
	-40°F						
Tensile Modulus, Type I $\frac{1}{8}$ " thickness (2)	73°F	psi	D-638-61T 0.2"/min.	330,000	350,000	380,000	310,000
	160°F, 73°F and -40°F						
	-40°F						
Flexural Strength $\frac{1}{8}$ " x $1\frac{1}{2}$ " x 4" bar (1)	160°F	psi	D-790-61 0.05"/min.	5,400 9,900 17,300	6,800 11,000 17,500	7,700 11,800 18,100	5,500 9,200 15,100
	73°F						
	-40°F						
Flexural Yield Strength $\frac{1}{8}$ " x $1\frac{1}{2}$ " x 4" bar (1)	160°F	psi	D-790-61 0.5"/min.	240,000 360,000 420,000	250,000 370,000 410,000	300,000 400,000 440,000	210,000 330,000 360,000
	73°F						
	-40°F						
Flexural Modulus $\frac{1}{8}$ " x $1\frac{1}{2}$ " x 4" bar (1)	160°F	psi	D-790-61 0.5"/min.	108	108	112	104
	73°F						
Hardness $\frac{1}{8}$ " thickness (1)	73°F	Rockwell R	D-785-62 Method A				

TABLE A (continued)

Properties Reported values pertain only to natural resins; pigmenting may vary the properties	Condition	Units	ASTM Test Method	CYCOLON MEDIUM IMPACT ABS POLYMERS			SPECIAL ABS RESINS
				A	AH	DH	
Wear Index, Taber Volume Loss Method CS-17 Wheel, 1000g. weight	73°F 50% R.H.	%		AM For Injection Molding	High Heat	High Heat	EP—3510 Grey Only For Chrome Plated Parts
Deformation Under Load (1)	24 hr., 122°F 2000 psi	%	D-621-59	AE For Extrusion	Injection Molding	Injection Molding	Injection Molding
Thermal Coefficient of Linear Thermal Expansion		in./in./°C. in./in./°F.		0.51	0.54	0.37	0.53
Deflection Temperature, Unannealed $\frac{1}{8}$ " x $\frac{1}{4}$ " x 5" bar (1)	264 psi 66 psi zero load	°F. at 10 mils Deflection	D-696-44 Calculated D-648-56	8.3 x 10 ⁻³ 4.6 x 10 ⁻³	8.5 x 10 ⁻³ 4.7 x 10 ⁻³	7.2 x 10 ⁻³ 4.0 x 10 ⁻³	9.5 x 10 ⁻³ 5.3 x 10 ⁻³
Deflection Temperature, Annealed $\frac{1}{8}$ " x $\frac{1}{4}$ " x 5" bar (1)	264 psi 66 psi zero load	°F. at 10 mils Deflection	D-648-56	187 203 216	198 210 222	199 217 227	192 209 220
Thermal Conductivity		BTU/hr./ft. ² /°F./in. Cal/Sec/cm ² /°C/cm.	C-177-45	1.49 5.12 x 10 ⁻⁴	221 223 227	223 227 232	215 221 226
Flammability $\frac{1}{8}$ " x $\frac{1}{4}$ " x 5" bar (1)		in./min.	D-635-63	1.6	1.6	1.6	1.54 5.30 x 10 ⁻⁴ 1.5
Analytical Specific Gravity (1)	73°F		D-792-60T Method A	1.05	1.04	1.05	1.07
Water Absorption (2)	73°F	%	D-570-63	0.40	0.33	0.32	0.40
Mold Shrinkage (2)		in./in.	D-955-51	0.005	0.004	0.004	0.005

*The word "CYCOLAC" is a Registered Trade Mark.

A sufficient amount of the stabilizer combination is used to enhance the resistance of the ABS polymer to discoloration at elevated temperatures. Only a small amount is required. Effective resistance to discoloration is obtained when the amount of stabilizer combination is from 0.1 to 10% by weight of the polymer. Preferably, for best results, from 0.25 to 2% is used. In these combinations, the amount of organic phosphite should be from 0.05 to 5%, the amount of the polycyclic polyhydric phenol should be from 0.05 to 5%, and the amount of the epoxy compound should be from 0.01 to 5%, by weight of the ABS polymer. Preferably, from 0.25 to 2% organic phosphite, from 0.05 to 2% polyhydric polycyclic phenol, and from 0.25 to 2% epoxy compound are employed for best results.

These stabilizer combinations generally contain from 2.5 to 50 parts of organic phosphite, from 2.5 to 50 parts of epoxy compound, and from 0.5 to 50 parts polyhydric polycyclic phenol.

The stabilizer composition can be formed by simply mixing the individual ingredients in the dry state or in a suitable liquid medium. Usually the phosphite and epoxy fatty acid ester will serve as the solvent for the phenol. When the phosphite is not excessively sensitive to moisture, another helpful expedient is to prepare the stabilizer composition in the form of an aqueous emulsion. Such an emulsion can be added to a freshly made ABS polymer latex before the polymer is isolated from the latex by the usual procedures of coagulation or spray-drying. A "master-batch" technique can be utilized to provide both wet and dry combinations of the stabilizer composition with the ABS polymer in proportions for compounding into larger quantities of polymer to be stabilized.

ABS polymers are conventionally blended with additives such as fillers, pigments and lubricants. Appropriate pigments and fillers are, for example, flour, cotton, shredded or chopped cloth, talc, chopped canvas, paper pulp forms, asbestos, powdered mica, calcium carbonate, carbon, graphite, quartz, diatomaceous earth silica, fibrous glass, barytes, calcium silicate, iron, barium sulfate, litharge, clay and titaniumdioxide. Fillers are normally used in an amount of from 2 to 40% by weight of the polymer. Typical lubricants are mineral oil, natural and synthetic waxes, fatty acids such as stearic acid, alkaline earth and heavy metal stearates, and aliphatic alcohols, ketones, and esters having from 16 to 60 carbon atoms in the molecule, including stearyl alcohol, palmitone, behenone, oleone, cetyl palmitate, in amounts of from 0.2 to 3% of the polymer.

If a combination of stabilizers is to be used, it may be formulated as a simple mixture for incorporation in the ABS polymer by the polymer manufacture or by the converter. An inert organic solvent such as xylene, cyclohexanone or ethyl benzene can be used to facilitate handling, if the ingredients do not form a homogeneous mixture or solution.

The following examples in the opinion of the inventors represent the best embodiments of their invention.

In the examples, the ABS polymer used was Cycolac T, a polymer of a mixture composed of 27% acrylonitrile, 20% butadiene, and 53% styrene. The three-component stabilizer system of the invention was evaluated against the stabilizing effect of each component thereof, taken singly and in pairs. The ABS polymer was pigmented by adding 3 parts of titanium dioxide to each 100 parts of the polymer, thus giving the unstabilized ABS polymer a creamy white initial colour. The stabilizers being tested were weighed and dispersed in the unstabilized ABS polymer on a two-roll laboratory mill and fluxed at a temperature of 280 to 300°F. for two to three minutes. The milled sheets were smooth and had dull surfaces. The sheets were then cut in strips, tested for resistance to deterioration when heated in an air oven at 350° or 375°F. Samples were withdrawn at 15 minute intervals and examined for discoloration. The discoloration was then rated visually by colour and numerically by colour number, according to the following standard colour scale:

COLOR NUMBER SCALE

Colour Number	Stages of Noticeable Difference in Colour
0	No discolouration from original
1	First noticeable discolouration from original
2	First noticeable discolouration from 1
3	First noticeable discolouration from 2
4	First noticeable discolouration from 3
5	First noticeable discolouration from 4
6	First noticeable discolouration from 5

5 The above table is based on the colour change of a non-stabilized standard polymer, which develops a further noticeably intensified discoloration in each fifteen minute heating period when heated at 350°F. At 375°F., this discoloration is more prominent and more rapid, so that the sample having improved resistance to discoloration when heated will not develop a noticeably different discoloration in each heating period but will discolour more slowly, and will tend to retain a given colour over one or more heating periods. Thus, a relatively stable sample after 30 to 45 minutes of heating may well retain a colour number maximum of 2 or 3, as compared to 5 for the standard sample. Thus, the colour number is a direct measure of the heat stability, vis-à-vis the colour standard.

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Example 1.

15 A stabilizer composition was prepared composed of 2,2-methylene-bis(4-methyl-6-nonylphenol), 2,6 - bis(2 - hydroxy - nonyl - 5 - methylbenzyl) - p - cresol, tris - (nonylphenyl) phosphite, and epoxidised soyabean oil. This system was employed to stabilize an acrylonitrile-butadiene-styrene polymer, as noted above, with and without the addition of titanium dioxide as a pigment. As controls, the individual stabilizer components were used, as well as the three pairs of these stabilizers, and a sample without any stabilizer. The test results obtained after oven ageing a 375°F are shown in Table I.

15

TABLE I

Stabilizer and Amount	None		A 1 part		B 1 part		C 1 part	
	None	TiO ₂ 3 parts	None	TiO ₂ 3 parts	None	TiO ₂ 3 parts	None	TiO ₂ 3 parts
Pigment								
Time (minutes)								
0	0	0	0	0	0	0	0	0
15	3	2	2	3	1	1	2	2
30	4	4	3	4	3	2	3	4
45	5	5	4	4	4	5	4	5

A: 2,2-methylene bis(4-methyl-6-nonylphenol) and 2,6-bis(2-hydroxy-nonyl-5-methylbenzyl)-p-cresol mixture.

B: Tris(nonylphenyl) phosphite.

C: Epoxidized soybean oil.

TABLE I (Continued)

Stabilizer and Amount	A 0.5 part B 0.5 part		A 0.5 part C 0.5 part		B 0.5 part C 0.5 part		A 0.25 part B 0.55 part C 0.20 part	
	None	TiO ₂ 3 parts	None	TiO ₂ 3 parts	None	TiO ₂ 3 parts	None	TiO ₂ 3 parts
Pigment								
Time (minutes)								
0	0	0	0	0	0	0	0	0
15	2	2	1	1	1	2	1	1
30	3	4	2	3	3	3	2	2
45	5	5	4	4	4	5	3	3

The results show the synergistic effectiveness of the stabilizer system of the invention. The phenol (A) provides only a slight improvement in the natural polymer, and replaces the yellow discoloration of the unstabilized TiO_2 pigmented polymer by a reddish discoloration of greater intensity. The phosphite (B) by itself is helpful in diminishing discoloration of the pigmented polymer but does little for the natural. The epoxy compound (C) presents the opposite behaviour, of being helpful in the natural polymer and ineffective in pigmented polymer. The pair AB is actually worse than either of its components in both natural and pigmented polymer. The pair BC has a slight favorable effect in natural polymer compound to its individual components, but with TiO_2 it is no better than the unstabilized pigmented polymer. The pair AC suffers from an unfavorable effect on the initial (unheated) colour of the natural polymer. Only the three-component system (ABC) is effective with both natural and pigmented polymer and in fact diminishes the discoloration at 375°F . to only that of an unstabilized polymer at 350°F .

Examples 2 to 8.

A number of stabilizer combinations were prepared, having the composition of stabilizers shown in Tables II and III. These stabilizer systems were combined with Blendex 435 ABS polymer, a transparent ABS polymer, 100 parts by weight, in the amount shown in the Tables, with and without TiO_2 pigment (3 parts), and the samples oven-aged at 375°F . The results are given in Tables II and III which follow.

In these Tables, the components of the stabilizer compositions are identified as follows:

- 1,1,3-TRIS: 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl) butane
- TPP: triphenyl phosphite
- MOPP: monoisooctyl diphenyl phosphite
- TNPP: tris-nonylphenyl phosphite
- RE 3,5: pentaerythritol(3,5-di-*tert*-butyl-4-hydroxy-phenyl)propionate
- 4,4'-THIO: 4,4'-thiobis-6-*tert*-butylmetacresol
- 4,4'-B: 4,4'-butylidene-bis-6-*tert*-butylmetacresol
- 2,2'-M: 2,2'-methylene-bis(4-methyl-6-*tert*-butyl-phenol)
- 1,3,5-T: 1,3,5-trimethyl-2,4,6-tris-(3,5-di-*tert*-butyl-4-hydroxy benzyl) benzene
- ESO: Epoxidized soyabean oil
- BIS A: Bisphenol A-glycidyl ether, epoxy equivalent 180—195
- BIS E: Bisphenol A-glycidyl ether, epoxy equivalent 550—700.

TABLE II (Not Pigmented)

At 375° F

Example No.	2	3	4	5	6	7	8
Time (minutes)	1,1,3-TRIS 0.1 TNPP 0.6 ESO 0.3	1,3,5-T 0.1 TNPP 0.6 ESO 0.3	PE 3,5 0.1 TPP 0.6 ESO 0.3	4,4-THIO 0.3 MOPP 0.4 ESO 0.3	4,4-B 0.3 MOPP 0.4 BIS E 0.3	2,2-M 0.3 BIS A 0.3 MOPP 0.4	Stabilizer 1.0 of Example 1
0	0	0	0	0	0	0	0
15	1	1	1	1	1	1	1
30	2	2	2	1	2	1	3
45	3	3	4	3	3	2	4

TABLE III (Pigmented with TiO₂)

At 375° F

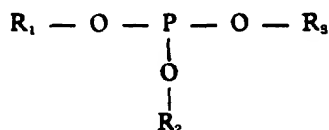
Example No.	2	3	4	5	6	7	8
Time (minutes)	1,1,3-TRIS 0.1 TNPP 0.6 ESO 0.3	1,3,5-T 0.1 TNPP 0.6 ESO 0.3	PE 3,5 0.1 TPP 0.6 ESO 0.3	4,4-THIO 0.3 MOPP 0.4 ESO 0.3	4,4-B 0.3 MOPP 0.4 BIS E 0.3	2,2-M 0.3 BIS A 0.3 MOPP 0.4	Stabilizer 1.0 of Example 1
0	0	0	0	0	0	0	0
15	1	1	1	1	1	1	1
30	2	2	2	1	2	1	3
45	3	3	4	3	3	2	4

The data show the stabilizer compositions to be effective in unpigmented and pigmented ABS polymer.

WHAT WE CLAIM IS. —

1. An acrylonitrile-butadiene-styrene polymer having its resistance to deterioration when heated at 350°F and above and enhanced by an amount of from 0.1 to 10% by weight of the polymer of a stabiliser combination comprising a polyhydric polycyclic phenol, an organic phosphite, and an epoxy compound the organic phosphite and epoxy compound each being in an amount of from 2.5 to 50 parts by weight, and the phenol being in an amount of from 0.5 to 50 parts by weight, the amount of each being selected within such ranges to enhance the stabilising effectiveness of the others.

2. An acrylonitrile-butadiene-styrene polymer as claimed in claim 1 in which the organic phosphite is an organic triphosphate having the formula

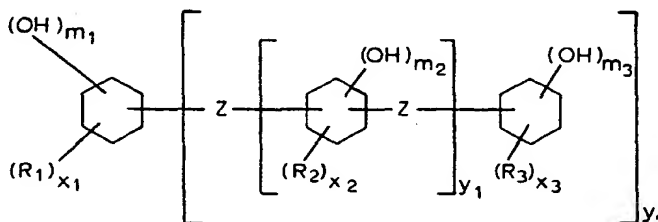


- in which R_1 , R_2 and R_3 are selected from alkyl, aryl, cycloalkyl, arylalkyl, alkylaryl, alkylcycloalkyl and cycloalkylalkyl groups having from one to thirty carbon atoms; the positions not substituted by organic groups contain hydrogen atoms.

3. An acrylonitrile-butadiene-styrene polymer as claimed in claim 1 or 2 in which the epoxy compound is a mono or polyhydric aliphatic alcohol ester of a fatty acid and has from 10 to 150 carbon atoms.

4. An acrylonitrile-butadiene-styrene polymer as claimed in claim 3 wherein the epoxy fatty acid ester is epoxidised soyabean oil.

5. An acrylonitrile-butadiene-styrene polymer as claimed in any of claims 1 to 4 wherein the polyhydric polycyclic phenol has the formula



- wherein R_1 , R_2 and R_3 are inert substituents selected from a halogen atom or organic radicals containing from one to thirty carbon atoms selected from alkyl, aryl, alkenyl, alkaryl, aralkyl, cycloalkenyl, cycloalkyl, alkoxy, aryloxy, acyloxy, carboxyl or thiohydrocarbon group, Z is an oxygen or sulphur atom or an alkylene, alkenylene, alicyclene, arylene, mixed alkylene-arylene or alkylene-alicyclene group, m_1 and m_3 are integers from 1 to 5, and m_2 is an integer from 1 to 4, x_1 and x_3 are 0 or integers from 1 to 4, and x_2 is 0 or an integer from 1 to 3, y_1 is 0 or an integer from 1 to 6 and y_2 is an integer from 1 to 5.

6. An acrylonitrile-butadiene-styrene polymer as claimed in claim 5, wherein Z is a sulphur atom.

7. An acrylonitrile-butadiene-styrene polymer as claimed in claim 5 wherein Z is an alkenylene group.

8. An acrylonitrile-butadiene-styrene polymer as claimed in claim 5 wherein Z is an alkenylene group.

9. An acrylonitrile-butadiene-styrene polymer as claimed in any of claims 5 to 8, wherein R_1 , R_2 and R_3 are alkyl substituents.

10. An acrylonitrile-butadiene-styrene polymer as claimed in any of claims 1 to 9 wherein the amount of phosphite is from 0.05 to 5%, the amount of epoxy fatty acid ester is from 0.05 to 5% and the amount of polycyclic polyhydric phenol is from 0.01 to 5%.

11. An acrylonitrile-butadiene-styrene polymer as claimed in claim 1 substantially as described with reference to any of the Examples.

12. A process for improving the resistance of acrylonitrile-butadiene-styrene polymers to deterioration when heated at 350°F which comprises incorporating in the poly-

mer a stabiliser combination as defined in claim 1 in an amount from 0.1 to 10% by weight of the polymer

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